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| (21) International Application Number: PCT/US97/16121 (22) International Filing Date: 18 September 1997 (18.09.97) (30) Priority Data: 60/029,814 30 October 1996 (30.10.96) US (71) Applicant: CYTEC TECHNOLOGY CORP. [US/US]; Suite 1052, 1105 North Market Street, Wilmington, DE 19801 (US). (72) Inventors: BINDER, Sidney; Apartment 1121, 71 Strawberry Hill Avenue, Stamford, CT 06612 (US). WU, Kuang-Jong; 55 Honeysuckle Hill Lane, Easton, CT 06612 (US). (74) Agents: SCHULTZ, Claire, M. et al.; Cytec Industries Inc., 1937 West Main Street, P.O. Box 60, Stamford, CT 06904-0060 (US). | | (81) Designated States: AL, AM, AU, AZ, BA, BB, BG, BR, BY, CA, CN, CU, CZ, EE, GE, GH, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, RO, RU, SD, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> |
| (54) Title: LIQUID CROSS-LINKER COMPOSITIONS CONTAINING 1,3,5-TRIAZINE CARBAMATE/AMINOPLAST RESIN MIXTURES | | |
| (57) Abstract High solids, liquid cross-linker compositions based on mixtures of 1,3,5-triazine carbamates and aminoplast resins and processes for preparing the same are disclosed. The liquid cross-linker compositions are particularly suited for use in formulating curable compositions such as high solids coatings compositions to be applied by spraying for use in automotive original equipment manufacture (OEM) and other related applications. | | |

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**LIQUID CROSSLINKER COMPOSITIONS CONTAINING 1,3,5-TRIAZINE
CARBAMATE/AMINOPLAST RESIN MIXTURES**

BACKGROUND OF THE INVENTION

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Field of the Invention

This invention relates generally to crosslinker compositions containing substantially homogeneous mixtures of 1,3,5-triazine carbamates and aminoplast resins and methods of preparation thereof. The invention also relates to a process for preparing curable coating compositions derived from the inventive crosslinker compositions as well as a method of coating substrates.

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Description of Related Art

Various derivatives of amino-1,3,5-triazines are described in the literature as having uses in a wide variety of fields. Certain of these derivatives, such as aminoplast resins including alkoxymethyl derivatives of melamine and guanamines, are useful as crosslinkers or reactive modifiers in curable compositions which contain resins having active hydrogen groups. See, for example, US4064191, US4081426, US4101520, US4118437, US4129681, US4243705, US4271277, US4276212, US4330458, US4374164, US4433143, US4425466, US4873298, US5155201, US5256713 and WO96/41826, all of which are incorporated herein by reference for all purposes as if fully set forth.

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While alkoxymethylated melamines and guanamines provide excellent results in a number of aspects, they also have the disadvantage of releasing formaldehyde as a volatile by-product under curing conditions. Crosslinking agents which minimize the release of formaldehyde but which also retain the advantageous performance characteristics of alkoxymethylated melamines and guanamines would be particularly advantageous and are highly desired.

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One promising non-formaldehyde emitting alternative is the class of isocyanate and carbamate functional 1,3,5-triazine crosslinking agents disclosed in US4939213, US5084541, US5288865, US5556971, US5565243, US5574103, EP-A-0624577, EP-A-0649842, WO96/04258, WO96/11915, WO96/15185 and WO97/08235, all of which are incorporated by reference herein for all purposes as if fully set forth. The aforementioned have been found to be particularly useful as crosslinkers in coating compositions based on active hydrogen and/or epoxy containing compounds, with the cured coatings possessing a wide range of desirable properties.

In a number of the previously incorporated references, it is disclosed that curable compositions containing polyfunctional active hydrogen and/or epoxy compounds and 1,3,5-triazine carbamate crosslinkers can be adapted for use in organic solvent-based coating compositions. For example, in previously incorporated US5574103 are disclosed organic solvent-based coatings prepared from organometallic, base or acid catalyzed systems using 1,3,5-triazine carbamate crosslinkers. Also disclosed therein is the use of the 1,3,5-triazine carbamates as co-crosslinkers in combination with conventional aminoplast resin crosslinkers to improve the acid etch resistance and lower formaldehyde emission of traditional organic solvent-based aminoplast resin crosslinked systems.

Solvent-based coating compositions are typically prepared by mixing a substantially homogeneous solution of the crosslinking agent in an appropriate organic solvent with the remaining ingredients. Due to the generally low solubility of 1,3,5-triazine carbamate crosslinking agents in most common organic solvents, however, only relatively low solids solutions of the 1,3,5-triazine carbamates can be used without precipitation problems during storage.

When these low solids solutions are utilized to formulate coating compositions, large amounts of unnecessary organic solvents may be introduced into the coating formulation, with the end result being that the organic solvent content of the final coating may be increased. Because of growing concerns regarding organic solvent emissions, this result is not desirable. Because 1,3,5-triazines carbamate crosslinkers impart a number of desirable properties to the final crosslinked films, a lower organic solvent containing alternative for use in formulating would be highly desirable.

An alternative approach is the use of 1,3,5-triazine carbamates in the solid state to prepare the above coating compositions directly without first preparing homogeneous 1,3,5-triazine carbamate solutions. This, however, has the disadvantage of being inconvenient to use, since it is generally more difficult to transfer solids than homogeneous liquids. Solid 1,3,5-triazine carbamates are also costly to manufacture. Furthermore, solid 1,3,5-triazine carbamates in general, and mixed solid 1,3,5-triazine carbamates in particular, may tend to cake out on storage, making them particularly difficult to transfer or dissolve.

In view of the adverse environmental impact of the VOC emissions and the difficulties associated with the use of 1,3,5-triazine carbamates in the solid form, there is a need for liquid, high solids and low VOC-containing 1,3,5-triazine carbamate crosslinker compositions which provide the end-user with the flexibility to use any many conventional coatings solvents and which can be conveniently prepared and used in curable

compositions such as coating compositions which can be adapted for application by conventional spray technologies commonly utilized in automotive original equipment manufacture (OEM) and other related applications. The present invention provides such liquid crosslinker compositions.

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SUMMARY OF THE INVENTION

The present invention meets the aforementioned industry need by providing a crosslinker composition comprising a liquid, substantially homogenous mixture of:

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- (i) a 1,3,5-triazine carbamate,
- (ii) an aminoplast resin and
- (iii) optionally an organic solvent,

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the crosslinker composition having a solids content of at least about 65 wt% based on the total weight of the crosslinker composition, the combination of (i) and (ii) comprising at least 50 wt% based on the total weight of the crosslinker composition, and the weight ratio of (i):(ii) being in the range of from 1:99 to 99:1. In addition to the above three components, the inventive crosslinker compositions may also contain other optional ingredients, for example, cure catalysts, light stabilizing additives, antioxidants, antifoaming agents and other additives and adjuvants normal to the particular chosen end use of the crosslinker composition, to the extent that the crosslinker composition remains within the above parameters.

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The present invention also includes a process for preparing a substantially homogeneous liquid crosslinker composition comprising the step of admixing a 1,3,5-triazine carbamate, an aminoplast resin and, optionally, an organic solvent at a temperature and for a length of time sufficient to produce said substantially homogeneous liquid crosslinker composition having a solids content of at least about 65 wt% based on the total weight of the crosslinker composition, the combination of (i) and (ii) comprising at least 50 wt% based on the total weight of the crosslinker composition, and the weight ratio of (i):(ii) being in the range of from 1:99 to 99:1.

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Also included is a liquid curable composition comprising a substantially homogenous mixture of (I) a resin component comprising a poly(active hydrogen and/or epoxy) compound; and (II) the substantially homogeneous liquid crosslinker composition described above. These curable compositions in accordance with the present invention may be utilized in a wide variety of fields as described in the a number of the previously incorporated references. A particularly preferred end use is as a one- or two-component

sprayable coating for elevated temperature cure applications such as, for example, automotive original equipment manufacture (OEM) pigmented basecoats and clearcoats.

These and other features and advantages of the present invention will be more readily understood by those skilled in the art from a reading of the following detailed description.

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DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The Crosslinker Compositions

The crosslinker compositions of the present invention are substantially homogeneous liquid compositions comprising a 1,3,5-triazine carbamate, an aminoplast resin and, optionally, an organic solvent. The crosslinker compositions in accordance with the present invention can be prepared using any combination and/or any ratio of the above ingredients provided that such combination produces a substantially homogeneous liquid composition meeting the parameters described above.

For clarification, the term "liquid" as used in the context of the present invention defines mixtures which are pourable at ambient temperature. Preferably such mixtures possess a viscosity of less than about 32,000 centipoise (cps) at 25°C, and more preferably a viscosity of less than 16,000 centipoise (cps) at 25°C, as measured by a Brookfield Viscometer in accordance with ASTM D2196.

The crosslinker compositions of the present invention are high solids compositions, containing a total solids of at least about 65 wt%, more preferably at least about 70 wt%, and especially at least about 75 wt%, based on the total weight of the crosslinker composition, as measured by ASTM D4713 (method B).

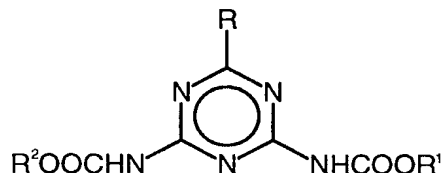
In one preferred embodiment, the inventive crosslinker compositions are substantially organic solvent free (at least 95 wt%, and preferably essentially 100 wt%, solids content), the aminoplast resin is a liquid aminoplast resin, and the weight ratio of 1,3,5-triazine carbamate to aminoplast resin is from about 1:99 to about 80:20, more preferably from about 1:99 to about 50:50, and especially from about 5:95 to about 25:75.

In another preferred embodiment, the inventive crosslinker compositions comprise an organic solvent in an amount up to about 35 wt% (and more preferably from about 10 to about 30 wt%), and from about 50 to about 90 wt% (and more preferably from about 65 to about 90 wt%) of the combination of the 1,3,5-triazine carbamate and the aminoplast resin, with the weight ratio of 1,3,5-triazine carbamate to aminoplast resin being from about 20:80 to about 99:1, and more preferably from about 25:75 to about 90:10.

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The 1,3,5-Triazine Carbamates

The 1,3,5-triazine carbamates suitable for use in the present invention are materials known from previously incorporated US4939213, US5084541, US5288865, US5556971, US5565243, US5574103, EP-A-0624577, EP-A-0649842, WO96/04258, WO96/11915, WO96/15185 and WO97/08235. Preferred for use in the present invention are those 1,3,5-triazine carbamates of the following general formula, as well as oligomers thereof:



wherein R is selected from the group consisting of -NHCOOR³, hydrogen, hydrocarbyl, hydrocarbyloxy, hydrocarbylthio, amido, sulfonamido, amino, hydrocarbylamino, dihydrocarbylamino and hydrocarbyleneamino (cyclic amino); and each R¹, R² and R³ is independently selected from a hydrocarbyl group.

The term "hydrocarbyl" in the context of the present invention, and in the above formula, broadly refers to a group which contains at least carbon and hydrogen atoms and includes, for example aliphatics, cycloaliphatics, aromatics and mixed character groups. "Hydrocarbyl" includes such groups as, for example, alkyl, cycloalkyl, aryl, aralkyl, alkaryl, alkenyl and cycloalkenyl, preferably having up to 20 carbon atoms. As exemplified below, these groups may also have a substituent group such as, for example, a hydroxyl, amino, halogen, cyano, sulfoxide, sulfone, carbonyl, ester and/or amide. As also exemplified below, these groups may contain a heteroatom in the chain, such as an oxygen, sulfur or nitrogen.

In more preferred embodiments, R is selected from -NHCOOR³; hydrogen; a hydrocarbyl having from 1 to 20 carbon atoms; a hydrocarbyloxy having from 1 to 20 carbon atoms (such as methoxy and phenoxy); a hydrocarbylthio group having 1 to 20 carbon atoms (such as methylthio and phenylthio); an amido group having from 1 to 20 carbon atoms (such as acetamido); a sulfonamido group having from 1 to 20 carbon atoms (such as benzene sulfonamido); an amino group; a hydrocarbylamino group having from 1 to 20 carbon atoms (such as methylamino, butylamino, methylolamino, methoxymethylamino and butoxymethylamino); a dihydrocarbylamino group wherein each hydrocarbyl group has 1 to 20 carbon atoms (such as dimethylamino, dibutylamino,

methylbutylamino, dimethylolamino, dimethoxymethylamino, dibutoxymethylamino, (methylol)(methoxymethyl)amino and (methoxymethyl)(butoxymethyl)amino); and cyclic amino groups having 3 to 20 carbon atoms (such as pyrrolidino, piperidino, morpholino and azepino). Preferred hydrocarbyls (as such or as part of other groups such as -oxy and -

5 amino groups) are alkyls having from 1 to 20 carbon atoms (e.g., methyl and butyl), aryls having from 6 to 20 carbon atoms (e.g., phenyl), cycloalkyls having from 4 to 20 carbon atoms (e.g., cyclohexyl), alkenyls having from 2 to 20 carbon atoms (e.g., vinyl) and aralkyls having from 7 to 20 carbon atoms (e.g., benzyl).

Still more preferred is when R is selected from -NHCOOR^3 , hydrogen, an alkyl of 1 to 20 carbon atoms, a cycloalkyl of 5 to 20 carbon atoms, an alkenyl of 3 to 20 carbon atoms, an aryl of 6 to 20 carbon atoms, an aralkyl of 7 to 20 carbon atoms and an amino group. Especially preferred is when R is -NHCOOR^3 .

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As preferred groups R^1 , R^2 and R^3 may be mentioned, for example, hydrocarbyl groups having from 1 to 20 carbon atoms such as alkyl (e.g., methyl and butyl), aryl (e.g., phenyl), cycloalkyl (e.g., cyclohexyl), alkenyl (e.g., vinyl), aralkyl (e.g., methyl phenyls), alkaryl (e.g., phenylmethyl), hydroxyalkyl (e.g., methylol), hydroxyaryl (e.g., hydroxyphenyl), alkoxyalkyl (e.g., methoxymethyl and butoxymethyl), aryloxyalkyl (e.g., phenoxymethyl), hydroxyalkoxyalkyl (e.g., hydroxypropoxymethyl) and hydroxyaryloxyalkyl (e.g., hydroxyphenoxymethyl).

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Particularly preferred of the above for R^1 , R^2 and R^3 are alkyls having 1 to 8 carbon atoms, alkenyls having 2 to 8 carbon atoms, cyclic alkyls and alkenyls having from 4 to 12 carbon atoms, alkoxyalkyls having from 2 to 16 carbon atoms, aryls having from 6 to 18 carbon atoms, aralkyls having from 7 to 20 carbon atoms and alkaryls having 7 to 20 carbon atoms. As specific preferred examples may be mentioned methyl, ethyl, propyl, n-butyl, i-butyl, t-butyl, pentyl, hexyl, cyclohexyl, heptyl, octyl, ethylhexyl, allyl, ethoxyethyl, hydroxyethoxyethyl, 1-methoxy-2-propyl, phenyl, 2-methyl phenyl, 3-methyl phenyl, 4-methyl phenyl and dimethylphenyls.

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Especially preferred 1,3,5-triazine carbamate crosslinkers for use in this invention are those of the above formula wherein R is -NHCOOR^3 , and wherein R^1 , R^2 and R^3 are independently an alkyl having 1 to 8 carbon atoms, and particularly methyl and/or butyl, which includes which includes tris-(butoxycarbonylamino)-1,3,5-triazine, tris-(methoxycarbonylamino)-1,3,5-triazine and tris-(methoxybutoxycarbonylamino)-1,3,5-triazine. As a preferred example of the latter may be mention such a 1,3,5-triazine carbamate crosslinkers having a methyl to butyl molar ratio in the range of from about 0.50

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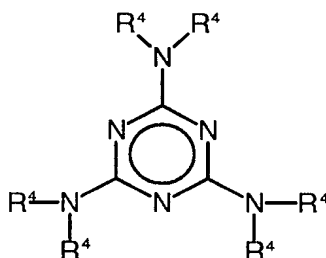
to about 1.5 (as determined by Nuclear Magnetic Resonance (NMR) spectroscopy), and particularly those having methyl to butyl ratios in the range of from about 0.65 to about 1.2.

These 1,3,5-triazine carbamates may be prepared, for example, by the methods described in the previously incorporated US4939213, US5084541, US5288865,
 5 US5556971, EP-A-0624577, EP-A-0649842, WO96/04258 and WO96/11915, and reference may be had thereto for further details.

The Aminoplast Resins

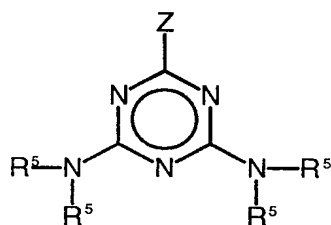
As suitable aminoplast resins may be mentioned the partially or substantially fully
 10 methylolated, partially or substantially fully etherified aminoplast resins based on melamine, guanamines, glycolurils and urea. In general, such aminoplast resins are well-known to those of ordinary skill in the art (see, for example, previously incorporated US5565243, US5574013, WO96/15185 and WO96/41826) and are generally commercially available. They include, most commonly, melamines, guanamines such as benzo-, aceto-, and
 15 cyclohexylcarbo-guanamines, glycolurils and ureas, as well as the at least partially N-alkylolated and N-alkoxyalkylated derivatives thereof. The term "aminoplast resin" also includes oligomers thereof.

As suitable melamine-based aminoplast resins may be mentioned those having the following general formula:



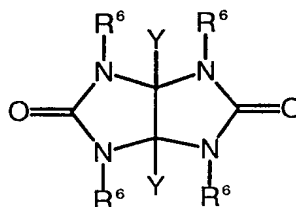
wherein each R⁴ is independently selected from H, an alkylol group and an alkoxyalkyl group. Preferred melamines are those wherein each R⁴ is independently selected from H,
 30 a methylol group and an alkoxymethyl group having from 1 to 8 carbon atoms in the alkoxy group.

As suitable guanamine-based aminoplast resins may be mentioned those of the following general formula:



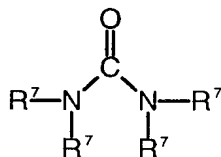
wherein Z is selected from H, an alkyl group of from 1 to 20 carbon atoms, an aryl group of from 6 to 20 carbon atoms, and an aralkyl group of from 7 to 20 carbon atoms, and wherein each R⁵ is independently selected from H, an alkylol group and an alkoxyalkyl group. Preferred guanamines are those wherein each R⁵ is independently selected from H, a methylol group and an alkoxymethyl group having from 1 to 8 carbon atoms in the alkoxy group, and particularly wherein Z is selected from a phenyl group (benzoguanamines), a methyl group (acetoguanamines) and a cyclohexyl group (cyclohexylcarboguanamines).

Suitable glycoluril-based aminoplast resins include those having the general formula:



wherein Y is selected from H, an alkyl group of from 1 to 20 carbon atoms, an aryl group of from 6 to 20 carbon atoms, and an aralkyl group of from 7 to 20 carbon atoms, and wherein each R⁶ is independently selected from H, an alkylol group and an alkoxyalkyl group. Preferred glycolurils are those wherein each R⁶ is independently selected from H, a methylol group and an alkoxymethyl group having from 1 to 8 carbon atoms in the alkoxy group.

As suitable urea-based aminoplast resins may be mentioned those of the following general formula:



wherein each R⁷ is independently selected from H, an alkylol group and an alkoxyalkyl group. Preferred ureas are those wherein each R⁷ is independently selected from H, a methylol group and an alkoxymethyl group having from 1 to 8 carbon atoms in the alkoxy group.

- 5 As specific examples of commercially available aminoplast resins of the type described above may be mentioned those sold under the trademarks CYMEL® and BEETLE® of Cytec Industries, Inc. (West Paterson, New Jersey).

The Organic Solvents

- 10 Organic solvents suitable for use in the crosslinker compositions of the present invention include common organic solvents including those described in the various incorporated references. Preferred are those solvents of the type typically found in coatings applications including, for example, alcohols, ketones, esters, ethers, amides, sulfones, aliphatic hydrocarbons, aromatic hydrocarbons, halogenated hydrocarbons and
15 the like, such as disclosed in previously incorporated US4939213, US5084541, US5565243, US5574103, WO96/15185 and WO97/08235.

- Particularly preferred organic solvents include ethers such as ethylene glycol dimethyl ether, diethylene glycol dimethyl ether and triethylene glycol dimethyl ether; amides such as N,N-dimethyl acetamide; N-methyl pyrrolidone; N,N-dimethyl formamide; hexamethyl
20 phosphoramidate; hydrocarbons such as toluene and xylene; sulfones such as dimethyl sulfone; sulfolane; esters such as methyl acetate, ethyl acetate and ethyl formate; and lower alcohols. Alcohols of 1 to 8 carbon atoms are preferred, and include methanol, ethanol, propanol, butanol, pentanol, hexanol, heptanol, octanol, isomers thereof and mixtures thereof. The most preferred alcohol is n-butanol. Solvents having a plurality of
25 functionalities such as ethylene glycol monomethyl ether, methoxypropyl acetate, hydroxypropyl acetate and the like, and mixed solvents, are also usable.

Other Optional Ingredients

- As indicated above, the inventive crosslinker compositions may also contain a variety
30 of other optional ingredients, for example, cure catalysts, light stabilizing additives, antioxidants, antifoaming agents and other additives and adjuvants normal to the particular chosen end use of the crosslinker composition.

 For example, cure catalysts for 1,3,5-triazine carbamate crosslinked systems, as exemplified by previously incorporated US4939213, US5084541, US5565243, US5574103,

WO96/15185 and WO97/08235, include acidic and organometallic catalysts of the type well-known to those skilled in the relevant coatings art.

As examples of acidic catalysts may be mentioned sulfonic acids (such as p-toluene sulfonic acid or dodecyl benzene sulfonic acid), aryl and alkyl acid-phosphates and pyrophosphates, carboxylic acids, sulfonimides and mineral acids. Latent acidic catalysts, such as amine-blocked p-toluene sulfonic acid, amine-blocked dodecyl benzene sulfonic acid, methyl p-toluenesulfonate, benzoin p-toluenesulfonate and the like are particularly useful as acid catalysts for producing compositions which are stable at room temperature and have a very long shelf life.

As examples of organometallic catalysts may be mentioned organotin compounds such as dibutyltin di-2-ethylhexoate, dibutyltin diisooctyl maleate, dibenzyltin di-2-ethylhexoate, dibutyltin dilaurate, dimethyltin dilaurate, tetrabutyl diacetoxystannoxane, tetramethyl diacetoxystannoxane, tetrapropyl diacetoxystannoxane, dibutyltin dichloride, and the like.

Combinations of the above mentioned catalysts are also suitable in the compositions of the present invention.

The cure catalyst, when used, should be present in the crosslinker compositions in an amount so as to result in a final formulated curable system containing from about 0.001 wt% to about 6 wt%, and preferably up to about 3 wt%, of the catalyst. Typically, this will result in the crosslinker composition comprising the cure catalyst in an amount up to about 15 wt %, and more preferably in an amount ranging from about 0.5 wt% to about 10 wt %, based on the total weight of the crosslinker composition.

Other optional ingredients may be additionally used depending on the particular application. For example, well known auxiliaries and additives typically utilized in the coatings industry include foam inhibitors, levelling aids, pigments, dispersants such as pigment dispersing aids, dyes, UV absorbers (including hydroxy aryl triazine types (such as CYAGARD® UV 1164 of Cytec Industries Inc.), benzotriazole types and benzophenone types), heat stabilizers, other stabilizing additives such as antioxidants, hindered amine light stabilizers (such as Sanduvor® 3055 and 3058 of Clariant) and the like. Other such optional ingredients have been exemplified in the many previously incorporated references, and reference may be had thereto for further details. Reference may specifically be had to US4426471, US4344876, US4619956, US5106891, US5322868, US5461151, EP-A-0434608, EP-A-0444323 and EP-A-0704437, all of which are incorporated by reference herein as if fully set forth, for detailed discussions of the stabilization of coatings

and other curable compositions with UV absorbers, hindered amine light stabilizers and/or other types of light stabilizers.

Preparation of the Crosslinker Compositions

5 The crosslinker compositions of the present invention are prepared by admixing a 1,3,5-triazine carbamate, an aminoplast resin and optionally an organic solvent and/or other optional ingredients, at a temperature and for a length of time sufficient to produce a substantially homogenous liquid crosslinker composition as described above.

10 In one embodiment, a solution of the 1,3,5-triazine carbamate in an organic solvent and an aminoplast resin and other optional ingredients are admixed. In another embodiment, neat 1,3,5-triazine carbamate and neat aminoplast resin are admixed directly, without solvent, and thereafter an organic solvent and/or other components are optionally admixed. In yet another embodiment, solid 1,3,5-triazine carbamate, an aminoplast resin and other optional ingredients (besides a solvent) are admixed, and thereafter an organic
15 solvent is optionally admixed. In still another embodiment, a solution of aminoplast resin in an organic solvent, the 1,3,5-triazine carbamate and other optional ingredients are all admixed.

20 The crosslinker compositions can also be prepared by further modifying a composition by increasing or decreasing the concentration of one or more components, for example, by admixing an additional amount of organic solvent or 1,3,5-triazine carbamate or by removing a portion of the solvent from any of the above crosslinker compositions or by sequentially carrying out both the admixing and the removing steps to produce a higher or lower solids crosslinker composition.

Preparation and Uses of the Coatings

25 The substantially homogeneous crosslinker compositions of the invention can be combined with a reactive resin component to form curable compositions suitable for numerous uses including, for example, as coatings and adhesives, in decorative laminated boards, and in the formation of crosslinked molded articles such as engineering
30 composites.

35 An especially preferred use of these curable compositions is in the coatings field. Liquid coating compositions can readily be prepared via methods and in relative amounts which are recognizable by those of ordinary skill in the art in the relevant field depending upon the particular end use chosen. As a general rule, the reactive resin component and the crosslinker component should preferably be admixed in the curable compositions in an

equivalents ratio (equivalents of reactive functionality) of from about 0.5:1 to about 2:1, and more preferably from about 0.8:1 to about 1.2:1.

Detailed discussions of suitable reactive resins can be found by reference to previously incorporated US4939213, US5084541, US5565243, US5574103, WO96/15185
5 and WO97/08235.

As preferred reactive resins for use in the coating compositions are compounds containing a plurality of active hydrogen and/or epoxy functionalities ("polyfunctional (active hydrogen and/or epoxy) resins").

Active hydrogen functionality, as utilized herein, refers to groups which contain active
10 hydrogens capable of reacting with, for example, the carbamate groups of the 1,3,5-triazine carbamates (or functionality which may be generated by the carbamate groups under cure conditions, such as isocyanate functionality), and/or with the imino, alkylol and/or alkoxymethyl groups of the aminoplast resins, under the cure conditions of the coatings.

Such active hydrogen functionalities are generally well known to those skilled in the
15 coatings art and includes groups such as hydroxyl, carboxyl, mercapto, amino, amido and carbamate groups. Preferred are hydroxyl, carboxyl and amino, and particularly hydroxyl. These groups are pendant from the backbone resins in the coating compositions of the invention and participate in the crosslinking process. The backbone resins are generally well known to those skilled in the art and are described in the previously incorporated
20 US4939213, US5084541, US5565243, US5574103, WO96/15185 and WO97/08235.

The preferred active hydrogen-containing resins are hydroxy group containing materials containing on average at least two, and preferably more than two, hydroxy groups per molecule. The preferred polyfunctional hydroxy group containing materials are acrylic or polyester backbone resins. Illustrative examples include acrylic resins which may
25 be obtained by the copolymerization of acrylic or methacrylic esters with hydroxyfunctional acrylic or methacrylic esters such as hydroxyethyl acrylate or methacrylate, optionally with simultaneous use of additional vinyl compounds such as, for example, styrene. Illustrative examples of the polyfunctional hydroxy group containing materials also include polyester resins which may be obtained, for example, by the reaction of polycarboxylic acids with
30 excess quantities of polyhydric alcohols. Additionally, suitable polyfunctional hydroxy group containing resins also include polyurethane prepolymers, alkyds, as well as hydroxy group containing epoxy prepolymers such as those resulting from the reaction of a polyfunctional epoxy group containing compound with an amine or with a polyfunctional carboxylic acid derivative. In general, the hydroxyl functionalities of such resins are pendent or
35 terminally attached, imparting the resins preferably the following characteristics: weight

average molecular weights (Mw) of from about 750 to about 7000, and more preferably from about 2000 to about 5000; and hydroxyl numbers of from about 20 to about 300 mg KOH/g resin and more preferably from about 60 to about 200 mg KOH/g resin.

Commercially available examples of active hydrogen containing resins include

- 5 DORESCO® TA 39-21 acrylic resin (Dock Resins, Linden, N.J.), JONCRYL® 500 acrylic resin (S.C. Johnson & Sons, Racine, WI), ACRYLOID® AT-400 acrylic resin (Rohm & Haas, Philadelphia, PA), CYPLEX® 1531 polyester resin (Cytec Industries, West Paterson, NJ), CARGILL 3000 and 5776 polyester resins (Cargill, Minneapolis, MN), TONE® polyester resin (Union Carbide, Danbury, CT), K-FLEX® XM-2302 and XM-2306 resins (King
10 Industries, Norwalk, CT), CHEMPOL® 11-1369 resin (Cook Composites and Polymers (Port Washington, WI), JONCRYL® 540 acrylic emulsion polymer (S.C. Johnson & Sons, Racine, WI), RHOPLEX® AC-1024 acrylic emulsion resin (Rohm & Haas, Philadelphia, PA), XC® 4005 water reducible acrylic resin (Cytec Industries, West Paterson, NJ), CRYLCOAT® 3494 solid hydroxy terminated polyester resin (UCB CHEMICALS USA, Smyrna, GA),
15 RUCOTE® 101 polyester resin (Ruco Polymer, Hicksville, NY), JONCRYL® SCX-800-A and SCX-800-B hydroxyfunctional solid acrylic resins (S.C. Johnson & Sons, Racine, WI), ALFTALAT® AN 745 hydroxyfunctional polyester resin, a product of Hoechst Corporation and the like.

- The polyfunctional epoxy compounds usable as the resin component in the curable
20 compositions of the present invention contain, on average, at least two and preferably more than two epoxy functionalities per molecule, and includes polyfunctional epoxy group containing materials which are monomeric, oligomeric, polymeric or a mixture thereof. Such polyfunctional epoxy compounds are in general well-known to those of ordinary skill in the art, as exemplified by US2872427, US3730930, US3752870, US3781380,
25 US3787521, US4011381, US4346144, US4607069, US4650718, US4681811, US4703101, US4764430, US4855386, US5001173, US5116892, US5118729, WO92/19660 and WO94/06876, all of which are incorporated by reference herein for all purposes as if fully set forth.

- As specific examples of monomeric polyfunctional epoxy compounds may be
30 mentioned difunctional epoxy resins (bisepoxides) including glycidyl ethers of dihydric phenols like the bisphenol-A/epichlorohydrin reaction products such as diglycidyl bisphenol-A; vinyl cyclohexene diepoxides such as 4-vinyl-1-cyclohexene diepoxide; 1,2,5,6-diepoxyoctane; 1,2,7,8-diepoxyoctane; dicyclopentadiene diepoxide; 1,4-divinyl benzene diepoxide; cyclohexene-4-methyl cyclohexene-4-carboxylate diepoxide;
35 glycidylated diol type polyfunctional epoxy group containing materials such as hexane diol

diglycidyl ether, ethylene glycol diglycidyl ether, diethylene glycol diglycidyl ether, triethylene glycol diglycidyl ether and the like. Other suitable monomeric polyfunctional epoxy compounds include trifunctional epoxy resins (trisepoxides) such as tri-(4-glycidyl oxyphenyl)methane and triglycidyl isocyanurate; and higher polyfunctional epoxides such as glycidylated pentaerythritol and sorbitol. As a commercially available example of bisphenol-A/epichlorohydrin reaction products may be mentioned epoxy resins sold under the trade designation Epon® of Shell Chemical Company (Houston, TX), such as Epon® 828 resin having an equivalent weight in the range of 185 to 192. As a commercially available example of a glycidylated sorbitol may be mentioned the substantially monomeric glycidylated sorbitol known as Synocure® 888 H resin (Cook Composites and Polymers Company, Port Washington, Wisconsin).

The oligomeric polyfunctional epoxy group containing materials include oligomeric forms of the monomeric materials, oligomers of diepoxides such as low molecular weight bis-phenol-A oligomers, prepolymers thereof, reaction products of amines with diepoxides, and the like.

The polymeric polyfunctional epoxy group containing materials include, for example, polymers of epoxy group containing unsaturated monomers and copolymers thereof with unsaturated comonomers which do not contain epoxy groups. As examples of the epoxy group containing unsaturated monomers may be mentioned glycidyl acrylate, glycidyl methacrylate and allyl glycidyl ether. As examples of the unsaturated comonomers which do not contain epoxy groups may be mentioned the alkyl esters of acrylic and methacrylic acid containing from 1 to 20 carbon atoms in the alkyl group, such as methyl acrylate, ethyl acrylate, butyl acrylate, ethylhexyl acrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate and ethylhexyl methacrylate; vinyl aromatic compounds such as styrene, methyl styrene and vinyl toluene; vinyl and vinylidene halides such as vinyl and vinylidene chlorides, vinyl esters such as vinyl acetate; allyl alcohol; and hydroxyalkyl acrylates and methacrylates containing from 1 to 20 carbon atoms in the hydroxyalkyl group, such as hydroxyethyl acrylate, hydroxyethyl methacrylate, hydroxypropyl acrylate, hydroxypropyl methacrylate and the like. The copolymerization reaction may be carried out by known methods such as that described in various of the aforementioned incorporated reference as well as in US3787521, US4181642, EP-A-0480120 and EP-A-0256369, which are also incorporated by reference herein as if fully set forth.

Commercially available examples of glycidyl methacrylate copolymer type polyfunctional epoxy group containing materials include Synthacryl® VCS 1436 resin a product of Hoechst-Celanese Corporation, Charlotte, NC; Estron® GMA-252 resin (Mw:

8300; EW: 250; Tg: 36), a product of Estron Chemicals, Calvert City, KY; Almatex® PD 6100 (Mw: 12500; EW: 1030; Tg: 63), Almatex® PD 6300, Almatex® PD 7110, Almatex® PD 7210, Almatex® PD 7310, Almatex® PD 7610 (Mw: 7000; EW: 510; Tg: 45) and Almatex® PD 1700 resins, products of Mitsui Toatsu Company, Inc. of Japan, and available
5 from Anderson Development Company, Adrian, MI; and Blemmer® CP-15 (Mw: 12300; EW: 1000; Tg: 63), Blemmer® CP-30 P (Mw: 10300; EW: 530; Tg: 62) and Blemmer® CP-5 SA (Mw: 10100; EW: 3000; Tg: 96) resins, products of Nippon Oil and Fat Corporation of Japan.

For waterborne applications, the polyfunctional materials may additionally have
10 thereon aqueous dispersion promoting groups such as carboxylic or sulfonic functionalities and higher molecular weights are generally usable, such as disclosed in previously incorporated WO96/15185 and WO97/08235, as well as GB1530022, EP-A-0568134, EP-A-0663413, US5075370 and US5342878, all of which are further incorporated by reference herein as if fully set forth.

For solvent borne coatings, a liquid resin component is generally preferred, however,
15 solid materials may also be used, particularly in cases when the solids are soluble in the particular formulation used.

In addition to the resin component, a 1,3,5-triazine carbamate, aminoplast resin and other optional ingredients, the coating compositions prepared by the process of the present
20 invention may optionally comprise a variety of additional ingredients. Depending on their end use, they may comprise other well known auxiliaries and additives typically utilized in the coatings industry including, for example, foam inhibitors, levelling aids, pigments, pigment dispersing aids, dyes, UV absorbers and other stabilizing additives, and the like. These other additives are discussed in general above, are well known to those skilled in
25 the relevant art and need not be discussed further.

The coatings of the present invention may be prepared by adding into a commonly used organic coatings solvent the components of the coating composition and the optional ingredients, if present, in any convenient order.

Any conventional type of coating may be prepared by any conventional method of
30 coating using the coating compositions described herein, including solvent based liquid coatings, waterborne coatings, high temperature coil coatings, and the like. For example, the present coating compositions may contain a solvent of the type typically found in coatings applications including alcohols, ketones, esters, aliphatic hydrocarbons, aromatic hydrocarbons, halogenated hydrocarbons and the like.

In liquid, organic solvent based coatings, the coating compositions are formulated to produce a solids content level suitable for convenient application with minimal material loss, preferably at a solids content level in the range of from about 20 weight percent to about 85 weight percent, and more preferably at a solids content level in the range of from about 45 weight percent to about 65 weight percent, depending on the method of application chosen.

The preferred method of application, as explained below, is by spraying, and one skilled in the art can, with the aid of the present description, formulate the coating compositions so as to be spray applicable.

Although the crosslinker composition and the active hydrogen containing material can be employed in varying amounts, when these components comprise the primary film-forming components of a subsequently formed coating, it is preferred that they be present in the coating compositions in amounts such that the molar ratio of the reactive functionality of the crosslinker component to the reactive functionality of the resin component is in the range of from about 0.5:1 to about 2:1, and especially in the range of from about 0.8:1 to about 1.2:1. When a plurality of functional resins and/or crosslinkers are employed, it is preferred that the overall reactive functionality ratio be within the above indicated ranges.

In actual practice, coating compositions containing a liquid medium such as a solvent and a substrate are contacted. Contacting may be carried out by dipping, spraying, padding, brushing, flowcoating, electrocoating or electrostatic spraying. After contacting, the solvent is allowed to partially evaporate to produce a uniform coating on the substrate. Thereafter, the compositions may be cured by further application of heat at a temperature and length of time sufficient to produce substantially fully cured coatings.

Preferably, cure temperatures are in the range of from about 25°C to about 450°C. In liquid coatings applications, the cure temperature is typically in the range of from about 80°C to about 160°C. In coil coatings applications, the cure temperature is typically in the range of from about 250°C to about 450°C. Cure time preferably is in the range of from about 1 second to about 30 minutes but may vary depending on the temperature chosen for cure. For example, a fully cured coil coating may be obtained by either curing at 260°C for 1 minute or by curing at 417°C for 20 seconds. Typical cure times for liquid coatings are in the range of from about 5 minutes to about 30 minutes.

Waterborne coatings can be prepared in a manner similar to that described in the previously incorporated WO96/15185 and WO97/08235, using the high solids, homogeneous crosslinker compositions of the present invention as the crosslinker

component. As described therein and above, the reactive resins suitable for use in waterborne coatings applications include those which possess sufficient anionic hydrophilizing functionality to render the curable coating composition water dispersible. The preferred hydrophilizing groups for most applications are those which generate anions upon neutralization and, particularly, the carboxyl and sulfonic groups. Especially preferred are carboxyl groups.

In order to render the active hydrogen-containing surface active resin water dispersible, the anion generating groups present on the resin must at least in part be neutralized. Suitable neutralizing agents for accomplishing this are well-known to those of ordinary skill in the art and include, for example, organic and inorganic bases such as sodium and potassium hydroxide, sodium and potassium carbonate, and amines such as ammonia, primary, secondary and tertiary amines. Tertiary amines are preferred.

Alternatively, waterborne coating compositions can be obtained by adding an aqueous dispersion-promoting material to the curable compositions of the present invention. Materials which qualify as aqueous dispersion-promoting materials can be readily identified by those skilled in the art. Preferred are an organic compound with such an alkyl chain or aromatic group substituted with the hydrophilic group. This includes, for example, long-chain aliphatic alcohols (e.g., ethylhexanol, octanol, dodecanol, and the like), benzyl alcohol and other aromatic alcohols, ester-alcohols (e.g., hydroxyalkyl esters of alkanolic acids), and the like. Especially preferred are the long chain alkyl alcohols having at least 8 carbon atoms, such as ethylhexanol, and hydroxyalkyl esters of alkanolic acids containing a total of at least 8 carbon atoms, such as a C₈-hydroxyalkyl esters of methylpropionic acid commercially available from Eastman Chemical Company under the trade designation Texanol®.

Method of Coating

The present invention further includes a method of coating substrates. The coating method comprises applying onto a substrate the coating compositions described above, and thereafter curing the so applied coating compositions to produce cured coatings and coated articles.

As mentioned above, any conventional coating method may be employed to prepare coatings, including methods such as roller-coating, dipping, and spraying. The especially preferred systems in accordance with the present invention are formulated for spray application.

The coating compositions of the present invention may be utilized in a wide variety of fields. A particularly preferred end use is as a one- or two-component coatings for elevated temperature cure applications such as, for example, automotive OEM clearcoats or pigmented basecoats. Other potential applications include, for example, coatings for wire, appliances, furniture, pipes, machinery and the like. Suitable substrates include glass, temperature resistant plastics, and metals such as steel and aluminum.

The foregoing discussion of the present invention will be further exemplified by the following examples offered by way of illustration and not as a limitation of the scope thereof.

EXAMPLE 1

Part A: Preparation of 1,3,5-Triazine Carbamate in n-Butanol

A mixture of 22.2 wt % sodium butoxide in n-butanol (219.5 lbs) and deaerated n-butanol (5 lbs) was placed in a 50 gallon glass lined reactor under an atmosphere of nitrogen, and a portion of the n-butanol (22 lbs) was distilled off. Deaerated dimethyl carbonate (32 lbs) was added with agitation while maintaining the temperature of the mixture at below 30°C. After one hour, deaerated melamine powder (14.5 lbs) was added and the slurry was heated at about 90°C for one hour. The reaction mixture was then cooled to 8°C, the pH adjusted to 6 using a combination of 5 N (106.5 lbs) and 2.9 N (9 lbs) nitric acid, and the resulting mixture was allowed to phase separate. The organic layer was filtered through a 0.5 micron filter to remove insolubles and washed with water (2 x 125 lbs). Sufficient volatiles were then removed to produce a product having the following characteristics:

| | |
|---|-------|
| Solids (Pan Solids Method, wt %) | 57.9 |
| Color (APHA method) | 500 |
| Haze (visual examination) | Clear |
| Residual Dibutyl Carbonate (GC, weight %) | 3.2 |
| Butyl Carbamate Content (%) | 64 |
| Methyl Carbamate Content (%) | 36 |

The methyl and butyl carbamate contents (%) of the 1,3,5-triazine carbamate were calculated from HPLC/MS analysis as follows. High pressure liquid chromatographic analysis (HPLC) showed the presence of seven major components in the 1,3,5-triazine carbamate sample (trisbutyl, bisbutyl-monomethyl, monobutyl-bismethyl, trimethyl, bisbutyl, monobutyl-monomethyl and bismethyl). Mass spectroscopic analysis (MS)

identified the various components, and hence, the number of methyl and/or butyl groups in each tris- or bis- derivative. After normalizing the sum of the HPLC area % values to 100% by first summing the area % values obtained from the HPLC analysis, and then multiplying each value by $1/(\text{Sum area } \%)$, the butyl content was calculated by summing the product of normalized area % value and the number of butyl groups for each component. Methyl content can be similarly calculated by summing the product of the normalized area % and the number of methyl groups for each component. The butyl and the methyl contents (%) of the mixture were calculated using the formulae (1) and (2): (1) % Butyl = $100 \times \text{Sum of Butyl} / (\text{Sum Butyl} + \text{Sum Methyl})$; (2) % Methyl = $100 - \% \text{ Butyl}$.

Part B: Preparation of Solid 1,3,5-Triazine Carbamate

The solution of Part A was diluted to 50 wt% in n-butanol, and 2150 g was placed in a round bottom flask attached to a rotary evaporator. Volatiles were removed under reduced pressure at 60-70°C until about an 80 wt% solids residue was obtained (approximately 900 ml distillate was collected). After addition of acetonitrile (8000 ml), the mixture was heated to about 90°C for 2 hours, after which the mixture was cooled to about 10°C (ice bath, 1 to 2 hr), and the solids were collected by suction filtration, washed with cold acetonitrile (3 x 500 ml), and vacuum-dried at 50°C to give the 1,3,5-triazine carbamate as a white powder.

Part C. Preparation of 1,3,5-Triazine Carbamate in n-Butanol (methyl:butyl ratio of 40:60)

A mixture of 25 weight % sodium methoxide in methanol (1774 lbs), sodium borohydride (205 grams) and deaerated n-butanol (3250 lbs) was placed in a 1000 gallon reactor under an atmosphere of nitrogen and most of the methanol was removed under reduced pressure with heating. An additional amount of deaerated n-butanol (3267 lbs) was added and the distillation was continued until about 3075 lbs of solution remained in the reactor. Deaerated dimethyl carbonate (592 lbs) was added with agitation while maintaining the temperature of the mixture at below 30°C. After one hour, the clear liquid was transferred to a mixing tank containing deaerated melamine powder (260 lbs) to form a uniform slurry and then the slurry was returned to the 1000 gallon reactor and heated at about 90°C for one hour. The reaction mixture was then cooled to 28°C, the pH adjusted to 5, and allowed to phase separate. The organic layer was filtered through a 0.5 micron filter to remove insolubles and washed with water (2 x 250 gallons). Sufficient volatiles were then removed to produce the following product:

| | | |
|----|--|-------|
| | Solids (Pan Solids Method, weight %) | 50.6 |
| | Color (APHA method) | 50 |
| | Haze (visual examination) | Clear |
| | n-Butanol (GC, weight %) | 46 |
| 5 | Residual Methanol (GC, weight %) | <0.1 |
| | Residual Dibutyl Carbonate (GC, weight %) | 0.8 |
| | Residual Dimethyl Carbonate (GC, weight %) | <0.1 |
| | Residual Methyl Butyl Ether (GC, weight %) | <0.1 |
| | Residual Dibutyl Ether (GC, weight %) | <0.1 |
| 10 | Butyl Carbamate Content (%) | 60 |
| | Methyl Carbamate Content (%) | 40 |

EXAMPLE 2

- 15 Homogeneous liquid crosslinker compositions were prepared by combining a 50 wt% solution of the solid 1,3,5-triazine carbamate (from Example 1, Part B) in n-butanol, a commercially available aminoplast resin crosslinker and an additional amount of solid 1,3,5-triazine carbamate (from Example 1, Part B) in the amounts shown in TABLE I. The appearance, viscosity and the final composition of the crosslinker compositions prepared in accordance with the present invention are also shown in TABLE I.
- 20

TABLE I

| | | A | B | C | D | E |
|----|--|-------|-------|-------|-------|-------|
| 5 | 50% solution of solid 1,3,5-triazine carbamate | 2.50 | 2.00 | 1.25 | 2.50 | 2.50 |
| | CYMEL [®] 303 Resin ⁽¹⁾ | 1.00 | 1.00 | 1.00 | ---- | ---- |
| | CYMEL [®] 301 Resin ⁽²⁾ | ---- | ---- | ---- | 1.00 | ---- |
| | CYMEL [®] 1135 Resin ⁽³⁾ | ---- | ---- | ---- | ---- | 1.00 |
| | Solid 1,3,5-triazine carbamate | 2.75 | 2.00 | 0.88 | 2.75 | 2.75 |
| 10 | Total | 6.25 | 5.00 | 3.13 | 6.25 | 6.25 |
| | Final Composition (wt%) | | | | | |
| | 1,3,5-triazine carbamate | 64 | 60 | 48 | 64 | 64 |
| | CYMEL [®] 303 Resin | 16 | 20 | 32 | ---- | ---- |
| | CYMEL [®] 301 Resin | ---- | ---- | ---- | 16 | ---- |
| 15 | CYMEL [®] 1135 Resin | ---- | ---- | ---- | ---- | 16 |
| | Non-volatiles | 80 | 80 | 80 | 80 | 80 |
| | Volatiles (n-BuOH) | 20 | 20 | 20 | 20 | 20 |
| | Viscosity (cps) | 9000 | 5600 | 1300 | 8600 | 5600 |
| | Appearance | | | | | |
| 20 | Initial | Clear | Clear | Clear | Clear | Clear |
| | After 1 Month at 5°C | Clear | Clear | ---- | Clear | Clear |

⁽¹⁾ CYMEL[®] 303 Resin is a product of Cytec Industries, West Paterson, N.J.

⁽²⁾ CYMEL[®] 301 Resin is a product of Cytec Industries, West Paterson, N.J.

25 ⁽³⁾ CYMEL[®] 1135 Resin is a product of Cytec Industries, West Paterson, N.J.

EXAMPLE 3

30 Two coating formulations were prepared by combining the ingredients set forth below. Formula F contains a 50 wt % solution of the solid 1,3,5-triazine carbamate in n-butanol (from Example 1, Part B) as the sole crosslinker, and formulation G contains Crosslinker Composition A of EXAMPLE 2 in accordance with the present invention.

| | FORMULATION | F | G |
|----|---|-------|-------|
| | DORESCO® TA 39-21 ⁽⁵⁾ (80%) | 97.32 | 94.54 |
| | 50% solution of solid 1,3,5-triazine carbamate | 44.29 | 0 |
| 5 | Crosslinker A (EXAMPLE 2, Table 1) | 0 | 30.45 |
| | CYCAT® 600 Catalyst ⁽⁶⁾ (10% in n-Butanol) | 10 | 10 |
| | Dow Corning Paint Additive 57 (1% in n-Butanol) | 5 | 5 |
| 10 | Arcosolv® ⁽⁷⁾ PM Acetate | 10.85 | 15.00 |
| | Methyl isobutyl ketone | 10.85 | 15.00 |
| | Xylenes | 10.85 | 15.00 |
| | n-Butanol | 10.85 | 15.00 |

15 ⁽⁵⁾ DORESCO® TA 39-21 acrylic resin is a product of Dock Resins, Linden, N.J.

⁽⁶⁾ CYCAT® 600 Cure Catalyst is a product of Cytec Industries, West Paterson, N.J.

⁽⁷⁾ Arcosolv® PM Acetate is a product of Arco Chemical Company.

20 The coating formulations were coated by wire cater applicator onto two Bondrite® 1000 treated cold rolled steel panels (Advanced Coating Technologies, Inc., Hillsdale, MI), and cured for 30 minutes at 140°C. The resulting cured films were tested for performance. Solvent resistance was measured by methyl ethyl ketone (MEK) double rubs "to mar" and "to remove" the coating. Highly crosslinked coatings require 200+ (i.e., more than 200) MEK rubs to mar. When two solvent resistance values are shown, the first is the number

25 of rubs to mar the coating, and the second is the number of rubs to remove the coating. When only one value is shown, the coating did not mar and the number shown is the number of rubs to remove it. The results are shown in the TABLE 2.

TABLE 2

| <u>Physical Properties of Coatings</u> | | F | G |
|--|--------------------------------------|--------------------|---------|
| 5 | Film thickness, mils | 1.5 | 1.5 |
| | Knoop hardness | 12.4 | 13.4 |
| | MEK double rubs | 200+ | 200+ |
| <u>Cleveland humidity resistance</u> | | | |
| 10 | Blistering, 2 days | 10 | 10 |
| | Blistering, 5 days | MB/D | MB/F |
| | Blistering, 9 days | MB/D | MB/F |
| | Blistering, 15 days | 5/D | 8/F |
| | Blistering, 21 days | 4/D | 8/M |
| | Blistering, 41 days | n/a | 8/D |
| 15 | KHN25, 0 days | 12.9 | 12.1 |
| | KHN25, 5 days | 12.2 | 11.9 |
| | KHN25, 9 days | 12.0 | 12.4 |
| | KHN25, 15 days | n/a ^(B) | 11.8 |
| | KHN25, 21 days | n/a ^(B) | 11.2 |
| 20 | MEK Rubs, 0 days | 200+ | 200+ |
| | MEK Rubs, 9 days | 10/200+ | 30/200+ |
| | MEK Rubs, 21 days | n/a ^(B) | 20/200+ |
| <u>Overbake Resistance, 160°C/60'</u> | | | |
| 25 | KHN25, before | 12.4 | 13.4 |
| | KHN25, after | 10.8 | 13 |
| | MEK double rubs, before | 200+ | 200+ |
| | MEK double rubs, after | 20/200+ | 200+ |
| <u>Water Immersion Test at 60°C</u> | | | |
| 30 | Appearance, 15 days | Clear | Clear |
| | Blistering, 15 days | 6/F | 10 |
| | MEK Rubs, 15 days | 2/170 | 20/200+ |
| | 20° Gloss (before MEK rubs), 15 days | 90 | 99 |
| | 20° Gloss (after MEK rubs), 15 days | 8 | 84 |

^(B) Film was not smooth enough to determine the property.

EXAMPLE 4

Homogeneous liquid crosslinker compositions H, I, J and K were prepared by combining solid 1,3,5-triazine carbamate (Example 1, Part B) and CYMEL[®] 301 aminoplast resin (100 % solids) or CYMEL[®] 303 aminoplast resin (100 % solids) or CYMEL[®] 1131 aminoplast resin (100 % solids) without solvent, in the amounts shown in TABLE 3, along with the appearance and the wt% of the 1,3,5-triazine carbamate in the final composition.

TABLE 3

| | H | I | J | K |
|--|-------|-------|-------|-------------|
| 1,3,5-Triazine Carbamate | 1.6 | 1.6 | 1.0 | 1.6 |
| CYMEL [®] 301 Resin | 9.0 | 0 | 0 | 0 |
| CYMEL [®] 303 Resin | 0 | 9.0 | 0 | 0 |
| CYMEL [®] 1131 Resin ⁽⁹⁾ | 0 | 0 | 9.0 | 9.0 |
| Wt% 1,3,5-Triazine Carbamate | 15% | 15% | 10% | 15% |
| Appearance | Clear | Clear | Clear | Slight Haze |

⁽⁹⁾ CYMEL[®] 1131 Resin is a product of Cytec Industries, West Paterson, N.J.

EXAMPLE 5

Homogeneous liquid crosslinker compositions L, M and N were prepared by combining a 50.6 weight % solution of a 1,3,5-triazine carbamate in n-butanol (from Example 1, Part C), CYMEL[®] 303 aminoplast resin (100 % solids) or CYMEL[®] 1131 aminoplast resin (100 % solids), and an organic solvent. The amounts used, the wt % of 1,3,5-triazine carbamate in the final composition, and the appearance of the final crosslinker composition are shown in TABLE 4. The initially prepared clear solutions remained clear for at least a month.

TABLE 4

| | | L | M | N |
|----|--------------------------|-----------------|-------|------------------|
| | 1,3,5-triazine carbamate | 42.5% | 40% | 42.5% |
| 5 | CYMEL® 303 Resin | 42.5% | - | - |
| | CYMEL® 1131 Resin | - | 40% | 42.5% |
| | Volatiles (n-BuOH) | 15% | 20% | 15% |
| | Viscosity (cps) | 9,500 | 500 | 2,415 |
| | Viscosity (G/H) | -Z ₅ | S | Z-Z ₁ |
| 10 | Appearance | | | |
| | Initial | Clear | Clear | Clear |
| | After 1 Month at 5°C | Clear | Clear | Clear |

15

EXAMPLE 6

20

A high solids, pourable, homogeneous liquid crosslinker composition O was prepared by combining a 50 wt % solution of a 1,3,5-triazine carbamate (prepared from the solid 1,3,5-triazine carbamate of Example 1, Part B and n-butanol), CYMEL® 303 aminoplast resin (100 % solids) and an additional amount of the solid 1,3,5-triazine carbamate (from Example 1, Part B) in the amounts shown in TABLE 5. The appearance, viscosity and the final composition of the high solids homogeneous liquid crosslinker composition is also shown in TABLE 5.

TABLE 5

O

| | | |
|----|--|-------|
| | 1,3,5-Triazine carbamate (50% in n-BuOH) | 3.33 |
| 5 | CYMEL® 303 Resin | 1.00 |
| | 1,3,5-Triazine carbamate (100 % solids) | 4.00 |
| | Total | 8.33 |
| | Final Composition (wt%) | |
| | 1,3,5-Triazine carbamate | 68% |
| 10 | CYMEL® 303 Resin | 12% |
| | Non-volatiles | 80% |
| | Volatiles (n-BuOH) | 20% |
| | Viscosity (cps) | 15500 |
| | Appearance | |
| 15 | Initial | Clear |
| | After 1 Month at 5°C | Clear |

Although the present invention is described with reference to certain preferred
embodiments, it is apparent that variations and modifications may be made by those skilled
in the art without departing from the scope of this invention as defined by the appended
claims.

CLAIMS:

1. A crosslinker composition comprising a liquid, substantially homogenous mixture of:

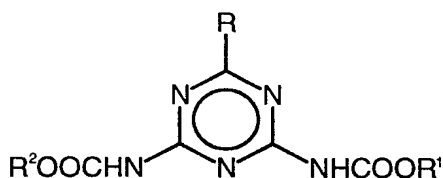
- (i) a 1,3,5-triazine carbamate,
- (ii) an aminoplast resin and
- (iii) optionally an organic solvent,

the crosslinker composition having a solids content of at least about 65 wt% based on the total weight of the crosslinker composition, the combination of (i) and (ii) comprising at least 50 wt% based on the total weight of the crosslinker composition, and the weight ratio of (i):(ii) being in the range of from 1:99 to 99:1.

2. The crosslinker composition of claim 1, having a solids content of at least about 95 wt% based on the total weight of the crosslinker composition, the aminoplast resin is a liquid aminoplast resin, and the weight ratio of (i):(ii) is from about 1:99 to about 80:20.

3. The crosslinker composition of claim 1, comprising from about 10 to about 30 wt% organic solvent and from about 50 to about 90 wt% of the combination of (i) and (ii), with the weight ratio of (i):(ii) being from about 20:80 to about 99:1.

4. The crosslinker composition of claim 1, characterized in that the 1,3,5-triazine carbamate has the following general formula:



wherein R is selected from the group consisting of -NHCOOR³, hydrogen, hydrocarbyl, hydrocarbyloxy, hydrocarbylthio, amido, sulfonamido, amino, hydrocarbylamino, dihydrocarbylamino and hydrocarbyleneamino; and each R¹, R² and R³ is independently selected from a hydrocarbyl group.

5. A liquid curable composition comprising a substantially homogenous mixture of (I) a poly(active hydrogen and/or epoxy) compound and (II) a crosslinker composition, characterized in that the crosslinker composition is as set forth in any one of claims 1-4.

- 5 6. A liquid, sprayable coating composition comprising a substantially homogenous mixture of (I) a poly(active hydrogen and/or epoxy) compound and (II) a crosslinker composition, characterized in that the crosslinker composition is as set forth in any one of claims 1-4.

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 97/16121

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08K5/3492 C08G59/50

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|---|-----------------------|
| A | WO 96 15185 A (CYTEC) 23 May 1996 cited in the application see examples 5,F,G; table 3 see examples 7,K; table 6 see claims 1-4,16-19,31 --- | 1,4,5 |
| A,P | WO 97 08235 A (CYTEC) 6 March 1997 cited in the application see page 21; claims 1,8,16; table 3 --- | 1,5 |
| A | EP 0 624 577 A (CYTEC) 17 November 1994 cited in the application see page 2, column 1 see claims 1,13 --- -/-- | 1,4 |

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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Date of the actual completion of the international search

16 December 1997

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INTERNATIONAL SEARCH REPORT

International Application No

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
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| Y | US 4 870 141 A (KORDOMENOS) 26 September 1989 see column 8, line 60 - column 9, line 29 see column 12, line 40 - line 46; claims 1,13,14 --- | 1,5,6 |
| Y | US 4 491 663 A (KORDOMENOS ET AL.) 1 January 1985 see column 2, paragraph 2; claims 1,7,11,13 --- | 1,5,6 |
| P,X | AMY ESSENFELD, KUANG-JONG WU: "A NEW FORMALDEHYDE-FREE ETCH RESISTANT MELAMINE CROSSLINKER" POLYMERIC MATERIALS SCIENCE AND ENGINEERING, vol. 77, 11 September 1997, LAS VEGAS, pages 385-386, XP002050294 see page 386, paragraph 2 --- | 1,4 |
| A | US 4 626 578 A (KORDOMENOS ET AL.) 2 December 1986 see column 10, line 30 - line 51; claims 1,15 ----- | 1,5,6 |

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Information on patent family members

International Application No

PCT/US 97/16121

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
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| EP 624577 A | 17-11-94 | AU 673908 B AU 6309794 A BR 9401969 A CA 2123469 A CN 1103641 A JP 7002804 A NO 941807 A | 28-11-96 17-11-94 13-12-94 15-11-94 14-06-95 06-01-95 15-11-94 |
| US 4870141 A | 26-09-89 | NONE | |
| US 4491663 A | 01-01-85 | NONE | |
| US 4626578 A | 02-12-86 | NONE | |